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by

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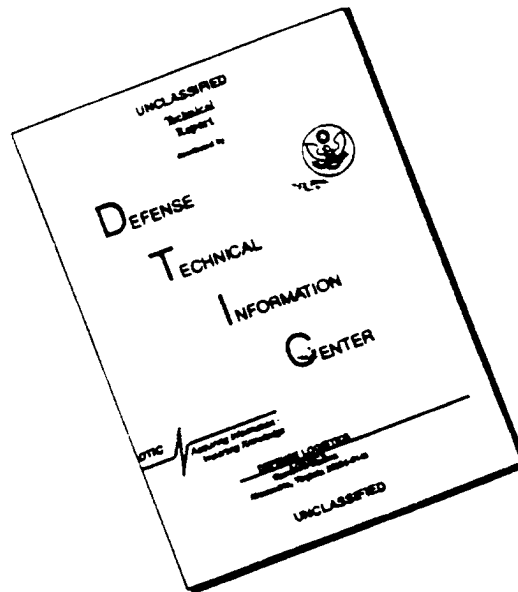
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Exciton Dynamics in Poly(p-pyridyl vinylene)

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Abstract

We present results of picosecond photoinduced absorption (PA) and time-resolved photoluminescence studies on solid and solution forms of poly(p-pyridyl vinylene). The nearly identical PA response of all forms of the polymer reflects the generation of the same primary photoexcitation, a Coulombically bound intrachain singlet exciton, and the absence of exotic species such as interchain excimers. The time dependence of the PA points to direct inter-system crossing as the origin of triplet excitons, ruling out generation of free carriers as a precursor to exciton formation.

78.47.+p,72.80.Le,71.35.+z

The suggestion that coulombically bound excitons are the primary photoexcitations of conjugated polymers has resulted in much debate and controversy, particularly in relation to arylene-vinylene-based polymers such as poly(p-phenylene vinylene) (PPV) [1–3]. Many different models have been proposed as to the nature of these excitons: Pakbaz et al. suggest that the Coulomb binding energy of the exciton is negligible, so that the primary photoexcitations of PPV are free carriers that later self-localize to form 'polaron-excitons' bound exclusively by the electron-phonon interaction [4]. Other authors suggest a Frenkel-or Wannier-like nature for the exciton, with a binding energy of several hundred meV [5–7]. Still others suggest strongly correlated excitons, with Coulomb binding energies on the order of 1 eV [8–11]. The issue of the nature of the exciton is of particular relevance because excitonic emission is thought to give the strong photoluminescence (PL) and electroluminescence seen in many conjugated polymers [12].

The debate over the primary photoexcitations in PPV and related systems has led to numerous ultrafast spectroscopic studies, again the interpretation of which has proven controversial. PPV shows strong, quasi-instantaneous photoinduced absorption (PA) at energies of ~1.5 eV [9,13–17]. Leng et al. [9] suggest that the strong PA arises from a transition from the lowest exciton state (S_1), and cite as evidence a correlation between the time dynamics of the PL and the time derivative of the PA (PL~ $d[\text{PA}]/dt$) at early times (<400 ps). Such a correlation might be expected if the PA were due entirely to singlet excitons, as PA(t) is proportional to exciton density and PL(t) to the rate of change of exciton density due to radiative recombination. They ascribe the discrepancy between PA and PL at later times to the trapping of excitons at defects [15]. On the other hand, Hsu et al. [16] take the discrepancy between PA and PL as evidence for photogeneration of a species distinct from the singlet exciton: namely 'polaron pairs,' or interchain excimers [18]. Yan et al. [17], citing an apparent competition between the PA and stimulated emission (SE), suggest that the quantum efficiency for polaron-pair generation is as high as 90 percent.

In this Letter, we address the nature of the PA in arylene-vinylene polymers via time-resolved studies on poly(p-pyridyl vinylene) (PPyV), the pyridine-based analog of PPV.

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The presence of a nitrogen heteroatom in the polymer repeat unit allows direct processing in solution and the casting of films. By considering the evolution of the PA, SE and PL as the PPyV sample is processed, we present strong evidence that, in all forms of the polymer, the PA at early times is due to singlet excitons, the same species that give the PL. We find no evidence for production of exotic species, such as polaron pairs, in any form of the polymer. Futhermore, we observe a second, long-lived component to the PA which we demonstrate originates from triplet excitons created via intersystem crossing from the singlet manifold. This secondary nature of triplet exciton production is in stark contrast to predictions of free-carrier models. The clear observation of triplet production is a result of the incorporation of nonbonding states into the conjugated backbone of PPyV which are not present in phenylene-based polymers such as PPV.

The picosecond time-resolved experiments were performed using 2.6-3.0 eV excitation from a cavity-dumped synchronously pumped dye laser that gave $\sim$ 5 ps, 0.1-10 nJ pulses at repetition rates of 250 kHz to 1 MHz. The PL was detected with $\sim$50 ps time resloution via time-correlated single photon counting techniques. PL decays were acquired to 10,000 counts in the peak channel. To eliminate the effects of spectral diffusion, for solid samples the time-resolved PL response was numerically integrated over energy by applying the trapezoidal rule. The PA was measured to $\sim$ 10 ps time resolution with a second dye laser (1.4-2.2 eV). The solution PA to 3.0 eV was also measured using a broad-band femtosecond system [19]. Poly(p-pyridyl vinylene) (PPyV) was obtained in powder form [20] and was dispersed in KBr (0.02% by weight) and pressed into pellets for study. Solutions (0.1-20 mg/mL) were prepared by dissolving the polymer in formic acid (HCOOH). Films were prepared by spin-casting or dropping concentrated solution onto glass or quartz substrates. The room-temperature powder and film measurements were performed in an evacuated cryostat and solution measurements in a spinning quartz cell.

Figure 1 displays the spectral response of the PA at 'zero' time delay for powder (open circles), solution (solid line and open squares) and film forms ($\times$) of PPyV. For reference, the PL and absorption spectra of a powder sample are shown. All forms show strong PA at

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1.5 eV. The solution and powder PA spectra display a crossover to SE above ~ 2 eV, which manifests itself as a negative signal (i.e., a positive $\Delta T/T$). No SE could be resolved below 2.2 eV in film samples. We suggest that the lack of SE in films is related to the formation of aggregate sites for the emitting excitons [21].

We first consider the nature of the PA in solution samples. Figure 2 displays the time dynamics of the PL at 2.5 eV (dotted line), PA at 1.4 eV (circles), and SE at 2.2 eV (diamonds). The PL decay is nearly single-exponential, with 90% of the decay accounted for by a $\sim$400 ps component. This single exponential behavior, together with a lack of Stokes shift between the PL emission and excitation spectra in solution [21], suggests that the primary photoexcitation in solution is a Coulomb-bound singlet exciton [2,22]. The PA is also nearly single-exponential for delays greater than 200 ps, and its similarity to the PL in this time domain indicates that *the PA and PL both arise from the same species: the singlet exciton*. In addition to the 400 ps component, the PA contains a fast component ($<$50 ps) which is outside of the temporal resolution of the PL measurement. The SE (diamonds) possesses an identical component, again suggesting the association of the PA with the singlet exciton. The marked deviation of the SE from the PA and PL after 400 ps is due to the onset of a second, long-lived PA, as is readily seen in the inset of Fig. 2. The contribution of this component to the 1.4 eV decay is apparently too small to be noticeable. The source of this long-lived signal is discussed below.

The spectral and temporal behavior of the PA and SE are independent of solution concentration over two orders of magnitude, indicating that both the short- and long-lived components arise from single-chain entities. Additionally, the dependence of the SE and PA signal on excitation wavelength follows the PL excitation profile at available pump wavelengths [21].

Next, we consider the results for powder samples. Figure 3 displays the energy-integrated PL decay (dotted line) and the PA decay at 1.4 eV (circles) for a PPyV/KBr powder sample. For comparison, the PA decay at 1.4 eV for a PPyV solution is also shown (triangles). Despite strong spectral diffusion in the PL decays [21,23], the energy-integrated PL decay

of the powder is nearly identical to that of the solution. The relationship between PA and PL in the powder samples is also the same as in solution: The PA follows the PL decay for delays between 200 and 700 ps, with a deviation at earlier times due to a fast PA component which is outside of the temporal resolution of the PL measurement. A further deviation at >700 ps is due to a second, long-lived state, discussed below. Interference from this long-lived state prevents comparison of the time dynamics of the SE (inset) and PA in powder samples.

Importantly, the solution and powder PA (triangles and circles, respectively) have essentially identical time dynamics for delays less than 1 ns, indicating that *the PA between 0 ps and 1 ns is due to the same species in both powder and solution: an intrachain singlet exciton.* Additionally, the powder PA and SE signals are linear in excitation intensity over an order of magnitude and have the same excitation spectrum as the PL over the available pump range [21]. In particular, we see no effects of 'competition' between PA and SE, as were previously observed in PPV [17]. Our results demonstrate that a substantially large PA signal can result from excitation from the lowest exciton state (S_1) in arylene-vinylene based polymers. We note that an analogous large PA signal has been seen for *trans*-stilbene, a model oligomer for the PPV system [24].

Next, we consider the origin of the long-lived signal. Figure 4 displays the PA dynamics at 1.9 eV for PPyV powder (squares) and solution (triangles). The powder signal shows an approximately exponential rise and decay, with time constants of ~230 ps and ~40 ns, respectively. The contribution of the long-lived component in solution is approximately one order of magnitude smaller than in the powder, in accord with the insets of Figs. 2 and 3. Comparison of the two curves demonstrates that the rise of the long-lived signal in the powder is correlated with the decay of the singlet exciton, as represented by the short-lived component in solution. The spectral response of the PA at 1 ns delay, shown in the inset of Fig. 4, is substantially different from that seen in Fig. 1, and in fact closely resembles that reported at millisecond time scales [25], (dotted line, inset), which has been shown to arise from triplet excitons. *We therefore suggest that the PA at 1 ns also is due to triplet excitons.*

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This conclusion is supported addit'   "· by the linearity of the 1 ns signal in excitation intensity, its persistence in dilute solution, and the extremely slow decay time of the signal.

As with the 0 ps PA, the excitation-wavelength dependence of the 1 ns signal follows that of the PL [21]. This fact, combined with the strong correlation between the decay time of the singlet PA and the risetime of the triplet PA and the linearity of the 1 ns PA in pump intensity, establishes that these triplets are generated by direct intersystem crossing from the singlet manifold. The slow rise of the triplet signal is in contrast to what one would expect if free carriers were the primary photoexcitation. In this scenario, triplet excitons would be generated in high quantum yield directly from uncorrelated electrons and holes, leading to a large, quasi-instantaneous PA similar to that of the singlets.

We propose that the dominance of the triplet signal at delays greater than 1 ns is indicative of enhanced triplet exciton production in PPyV powders over that of PPV. Such an enhancement is suggested to be mediated by the nonbonding (n,π^*) states associated with the nitrogen lone pair, as intersystem crossing from a (n,π^*) state to a (π,π^*) state is allowed to first order in the spin-orbit interaction [26]. Quantum chemical calculations [21] indicate that the lowest (n,π^*) states are located more than 1 eV above the lowest (π,π^*) states in the planar polymer [21] and should therefore not significantly alter the low-energy photophysics of PPyV with respect to PPV. However, deviations from planarity of the pyridyl rings can induce significant mixing between the (n,π^*) and (π,π) manifolds. Such nonplanarity is likely more abundant in the powder form than in solution, leading to the difference in intersystem crossing rates suggested by Fig. 4. [21].

Finally, we consider the results for film samples, shown in Fig. 5. The PL decay (dotted line) is distinctly nonexponential, which we suggest to result from migration of excitons to aggregate sites [21]. The PA decay at 1.4 eV (circles) deviates substantially from the PL decay; however, the PA closely follows the time integral of the PL, $\int_t^\infty PL(t')dt'$ (solid line) in accord with the relationship $PL \sim d[PA]/dt$. This correspondence again suggests the association of the PA with singlet excitons [9,21]. A second, long-lived response is evident in the 1.9 eV PA (squares), which we suggest to arise from triplets. The reduced triplet

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...... in film samples again points to the dependence of intersystem crossing rates on sample morphology.

As the PA in all forms of PPyV can be assigned as due exclusively to singlet and triplet excitons, substantial direct photogeneration of polaron pairs, as suggested by others for PPV [17,27], is ruled out in our samples. We therefore suggest that luminescence quenching due to polaron pair generation may not be a general phenomenon in arylene-vinylene-based conjugated polymers. High luminescence efficiencies in these systems may therefore be achievable through careful control of morphology.

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FIGURES

FIG. 1. Picosecond photoinduced absorption (PA) spectrum at 'zero' time delay for PPyV powder (open circles), solution (open squares) and film ($\times$); femtosecond PA spectrum (integrated to 10 ps) for solution (solid line). The photoluminescence (PL, dashed line) and absorption (abs, dot-dashed line) spectra of the powder sample are shown for reference. The dotted line is a guide to the eye.

FIG. 2. PA (1.4 eV, circles), PL (2.5 eV, dotted line) and stimulated emission (SE) (2.2 eV, diamonds) versus time delay for PPyV solution. Inset: SE/PA at 2.2 eV, shown on a linear scale.

FIG. 3. PA (1.4 eV, circles) and energy-integrated PL (dotted line) versus delay for PPyV powder. PA decay at 1.4 eV for PPyV solution (triangles) is shown for comparison. Inset: SE/PA at 2.2 eV, shown on a linear scale.

FIG. 4. PA at 1.9 eV vs. delay for PPyV powder (squares) and solution (triangles). Fit (solid line) is discussed in the text. Inset: PA spectrum at 1 ns delay (diamonds) for PPyV powder. Dashed line corresponds to millisecond PA spectrum.

FIG. 5. PA at 1.5 eV (circles), PA at 1.9 eV (squares) and energy-integrated PL (dotted line) vs. delay for PPyV film. The solid line represents $\int_t^\infty \text{PL}(t')dt'$.
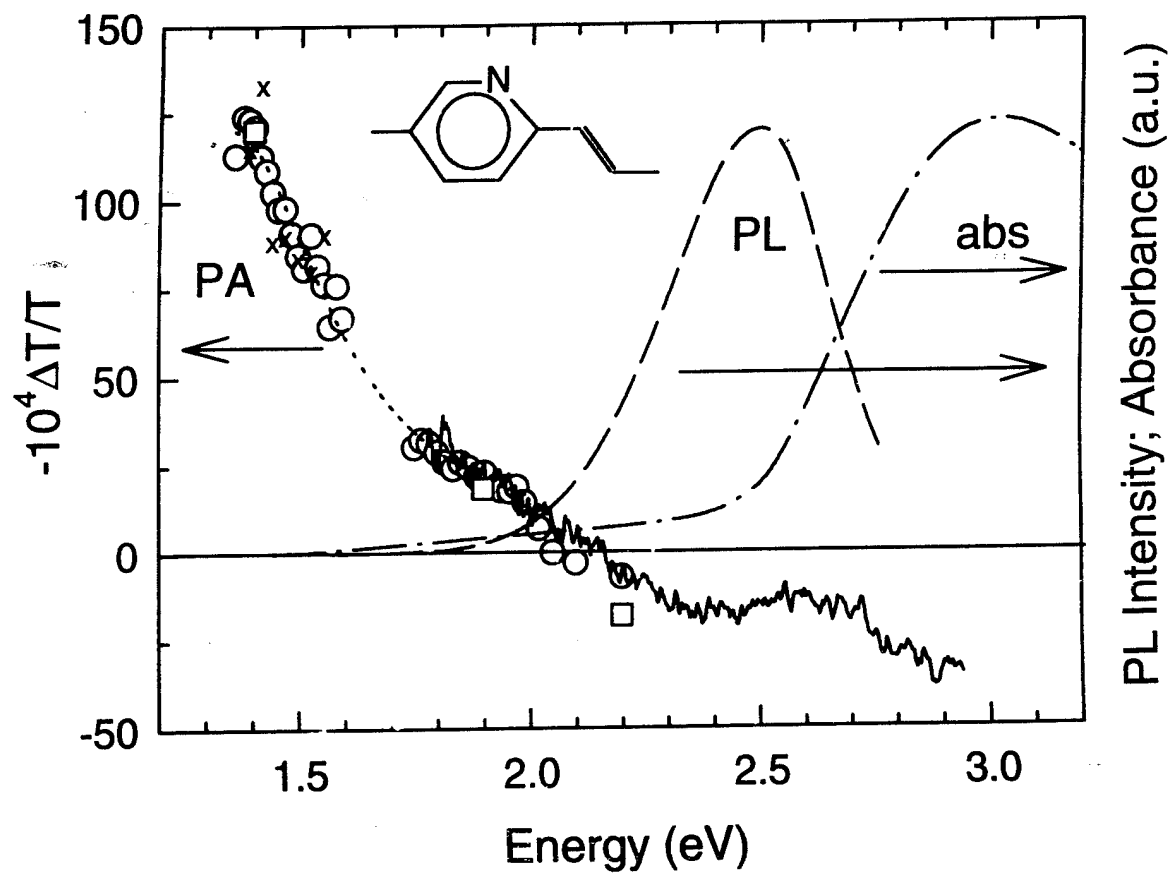
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Figure 1, Blatchford *et al.*
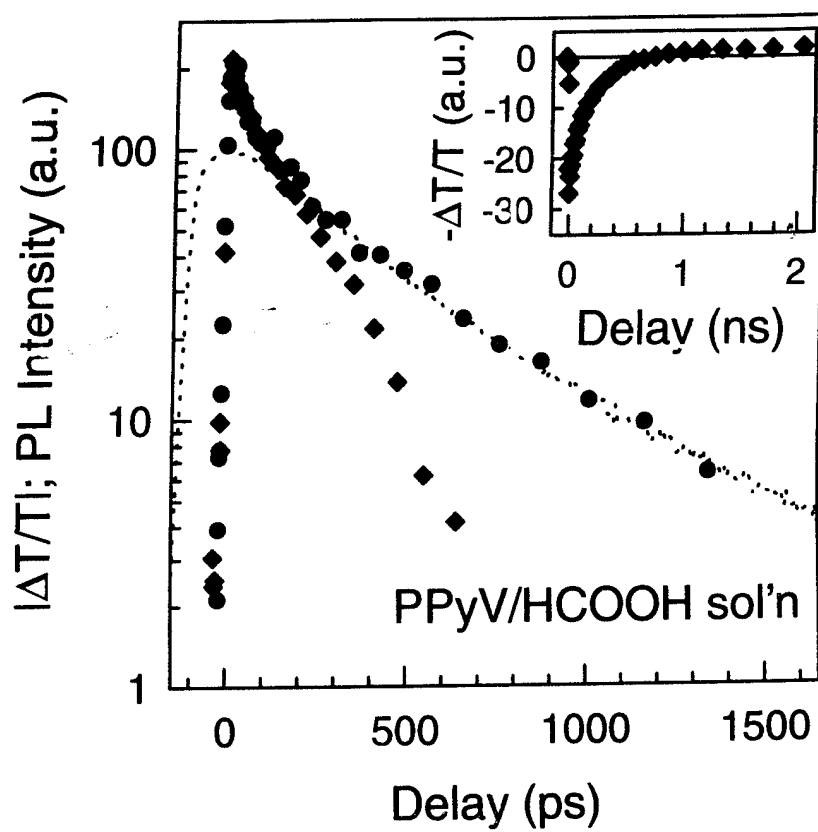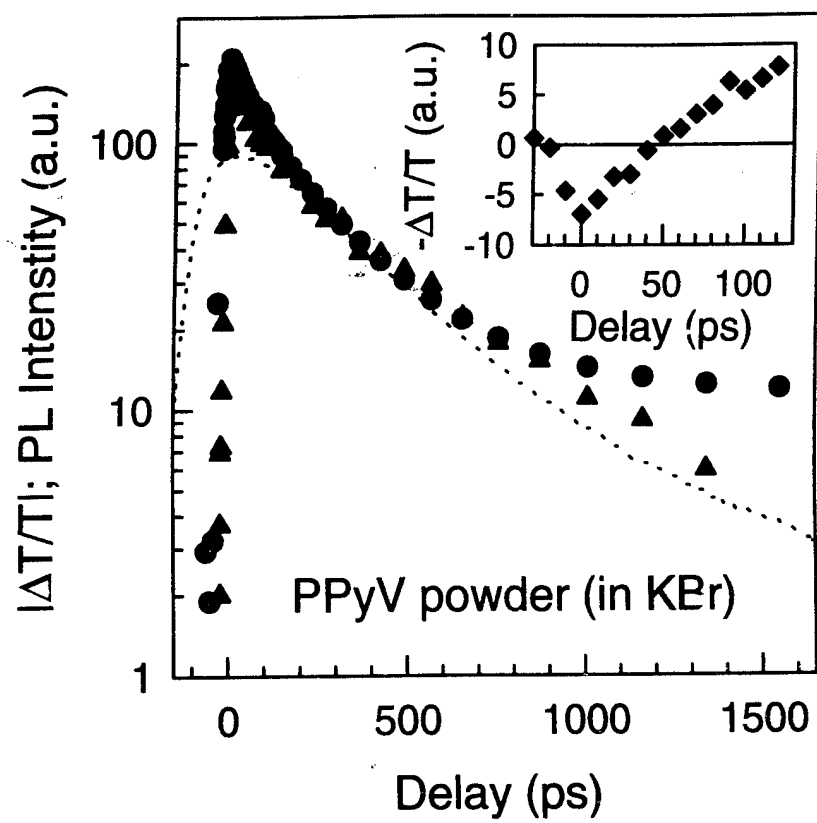
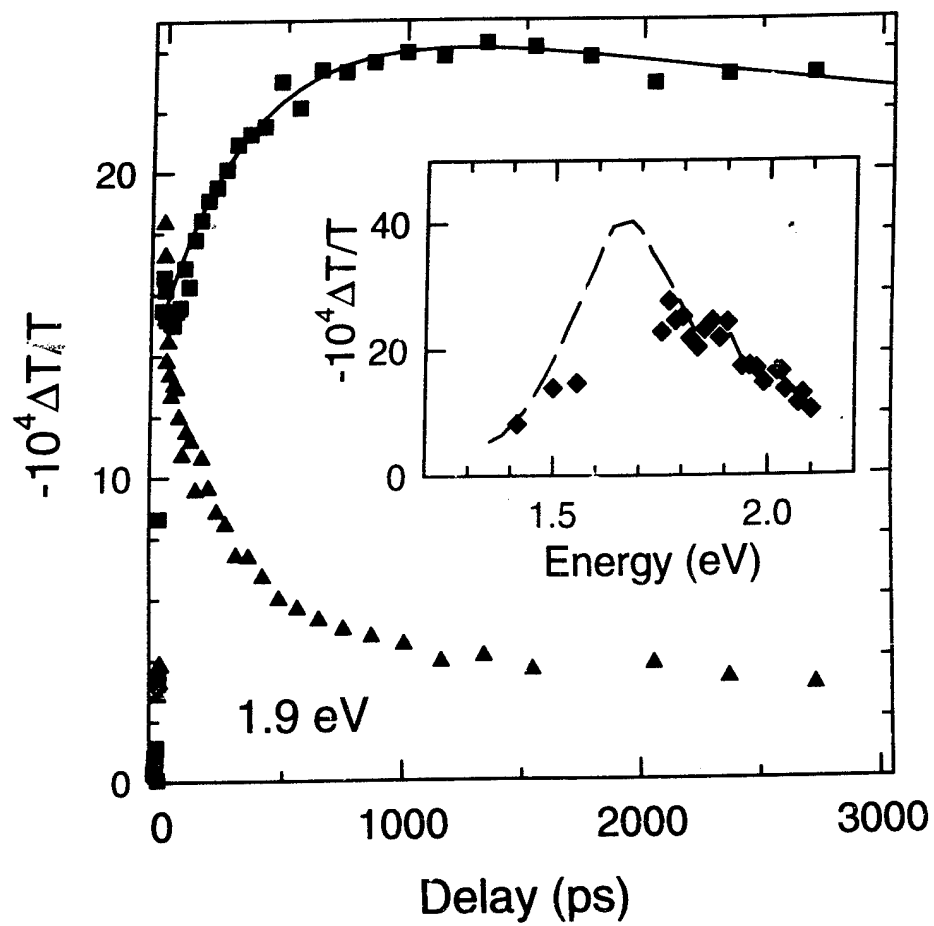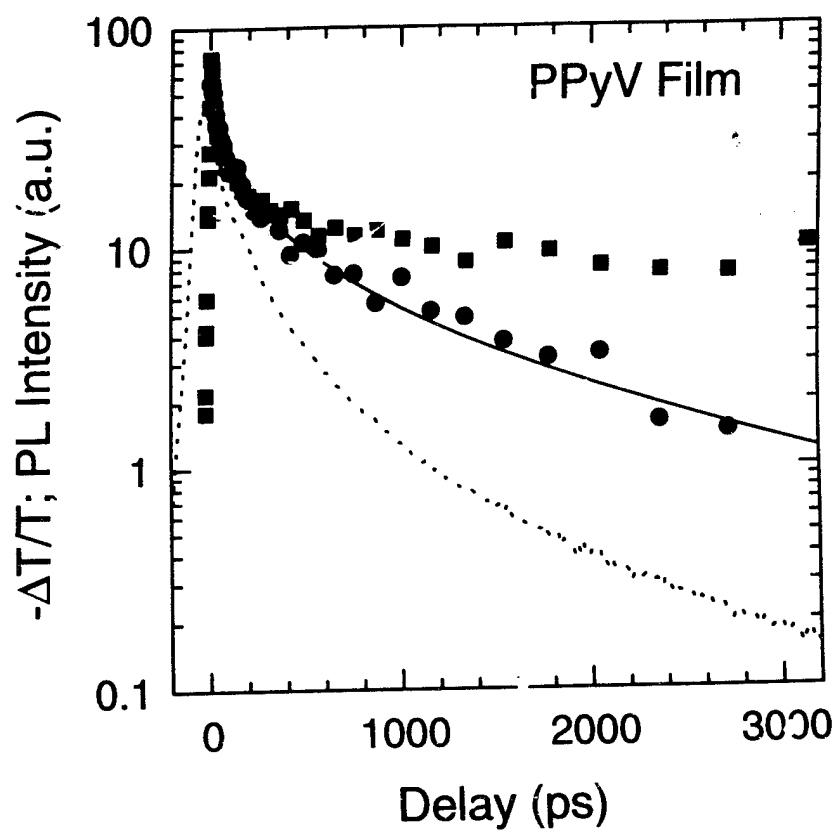Figure 2, Blatchford *et al.*

Figure 3, Blatchford *et al.*

Figure 4, Blatchford *et al.*

PPyV Film

Figure 5, Blatchford *et al.*